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(54) Title: METHOD FOR SELECTIVE ADSORPTION OF DIENES

(57) Abstract

The invention provides specific adsorbents and methods for separating an unsaturated hydrocarbon from a mixture containing such hydrocarbon. The adsorbents and methods are useful for separating dienes from mono-olefins. The adsorbents are selected from: a) an ion-exchanged zeolite selected from the group consisting of zeolite X, zeolite Y, and zeolite LSX, said zeolite having exchangeable cationic sites, and a plurality of said sites having silver cation or copper cation present; b) type A zeolite having exchangeable cationic sites, a plurality of said A zeolite sites having an alkali metal cation or an alkaline earth metal cation present.

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METHOD FOR SELECTIVE ADSORPTION OF DIENES FIELD OF THE INVENTION

The present invention relates to a process, and specifically selected adsorbents, for selective adsorption to separate a diene from a mixture, particularly one containing mono-olefin.

BACKGROUND OF THE INVENTION

In the preparation of commercial hydrocarbon product, it is often necessary to separate the desired product from other hydrocarbons having similar boiling points. For example, butene is synthesized commercially by processes which yield butadiene mixed with 1-butene. Conversely, butadiene product may also be contaminated with butene. Depending on the process used, the mixture may include other C3 and C4 hydrocarbon components including but not limited to 2-butene, other n-butenes, n-butane, isobutane, and isobutylene.

Purifying the mono-olefin, 1-butene, : is particularly troublesome due to closeness of its boiling point to that of 1,3-butadiene. In order to increase the purity of 1-butene, it is necessary to separate it from other hydrocarbons. Ordinarily, fractionation alone is incapable of completely separating 1,3-butadiene to achieve desired purity of the 1-butene mixtures. these Presently, butadiene is separated sfrom paraffins primarily by distillation with selective solvents by absorption using solutions of absorbents. Extractive distillation is relatively energy-intensive, complex and not economical. Selective absorption with metal salt solution involves a significant number of stages with recycling of streams between stages. This method has the disadvantage of being energy-intensive and requiring handling and recirculating of of solvent streams which themselves contain contaminants or are subject to to be Current processes degradation. for olefin\paraffin

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economically achieve the desired result for purifying Therefore, there mixtures of unsaturated hydrocarbons. remains the need for an improved method and improved adsorbents for use anima methods to effectively economically purify unsaturated hydrocarbons. That have a substitute of a substitution of the state of particulation execut for solective a bit blon of a bit blon throng about the grantmang time display and are very . I have the ្នាក់ ក្រសួងការពេលនៅ នៅក្នុងដោយស្រាយស្រាយស្រាយស្រាយ នៅក្នុងស្រាយ នៅក្នុងស្រាយ នៅក្នុងស្រាយ នៅក្នុងស្រាយ នៅក្នុ commencial provides methods and succession of the but there werediene analyty ortal dans " who tylinge out were and a preparation of the series of the charities o cono-quefin guin as butens "Britane Alam Man ed: 71.0 The State of the S Thene sad garg-cleftin composts d'esta often Vanha satte elignitéraceur l'abrassurai fil cluber à us mériseus s ರಾಜನಾಯಿಕರಾವಿಗೆ ಕೆರ್ಡಿಕ್ಸ್ ಸಿಟ್ ಕರ್ಮನ ಕರ್ಮಾಯ ಬರುಗೆ ಕರ್ಮನೆಗೆ ಗೆರು ಅಂಚಿತಮುತ್ತರು pauseicul von in in mississis do especia pai ou esposare adas ំ ១ ១ ១១៩៩៦ ០០០ វិទី១១,១១៩១២(វៀស្តី១១ មុទ្ធប្រទេសចិន្ត្រាម គឺមាន ១,១១៤៦០ ಕರಣರು ೧೯೫೪-೭೮೮ ೬- ೧೦ ಸಂಖ್ಯಾಗಾಧ್ಯಕ್ಷಕ ಅತರ ಗೆರವರ್ಗ ಅವಕಾಗಿಸಿದರು wassers and the second of the second ್ಟ ಕ್ಲಮ್ಮೆನ ಅಗುರತ್ತೆದ್ದ ಮೂಲಗಾಣ ಕಡೆದಲ್ಲಿ ಕೆಡ್ ಆರಾಹಿಗಳ Later Colored Colored 製造 デオールの対象 In the same of the same of the il Lioidgue, ាររំប្រ ខាន់ នោះ មានក្រោះ 1.5 အား မက္စားမည္းစရီး ျပည္သည္သည္သည့္ edo ko ကုန္သည္။ ကုန္သည္သည္ ျခစ္အလည္း ನಿನ ಪ್ರಸ್ತಿಕರಣಕ್ಕೆ ನಿಶ್ವ ಅಗಳುಗ್ಗಳಲ್ಲಿ ವಿಶ್ವಕ್ಷಿಗೆದಗಳು (ಹಿ. ೧೯೮೩) ಬಿಕ್ಕು ಕ್ಷತಿಗಳಿತ್ತೇನ್ನು ವೆಂದಿಗೇ ಸಹಾರೋಧಕಾತ ಎ.ಎ ಎರ. ೧ ಕಮ್ಮಾನ್ಯಕ್ಷ 🤾 ೧ Recording Statistics and the second second ್ರಾಟ್ ಮ್ ಪ್ರತಿಕ್ರಮ ವಿಧ್ಯಕ್ಷ ಕಟ್ಟಿಯ ಅತ್ಯ ಶ್ವರ್ಡಿಯ ಪ್ರ UI, STORMER LOOK BORELLY TORY ದು ಸಹಿತ ಕರ್ಷದೀರಿಯ ಗೆ ೧೨೦ ಗರಾವಿತ ಅದರ ಸ್ವಾಧಕ್ಷಗಳಿಕ ೫೯೧ ಗ್ರ ස 12 සංකෘතය මුලුව, මුල් පසු වේදන් දුම් පුසුවිල දෙදායුතු පලවාරයේ ඉදිනිස්තුරු ကိုး မေးသည်သို့နေရး ကြည်းကျည်သည်။ ကြည်မြောင်းများကျင်းကျွန်းသည်။ နောင်းသည်သည်။ ကြည်များများများ gu gga no jeudu na tulisand utilital neddon no mei'nie tafta colden aleberateden වැසියවෙන්න සා මූ විය. මිට් දුරු ජනතමට සා වට විසල සු Com විද්යාමය වඩා වට වුල් සු

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BULLY CONTROL STATE THE SUMMARY OF THE INVENTION

The invention provides new methods for separating unsaturated hydrocarbons from a mixture comprising the unsaturated hydrocarbons a The invention provides adsorbents specifically selected for accomplishing the separation. The absorbents and separation methods are particularly useful for selective adsorption of a diene from mixtures containing the diene; and are very effective for separating dienes from mono-olefins. In one aspect the invention provides methods and adsorbents to separate butadiene, hexadiene and/or octadiene from hydrocarbon mixtures; particularly where the hydrocarbon mixture contains a mono-olefin such as butene, hexane and/or octene.

Diene and mono-olefin compounds are often found together as a result of industrial processing. The separation of dienes from mono-olefin is difficult to achieve due to the closeness of their respective boiling points. This difficulty is illustrated by considering 1,3-butadiene, which has a boiling point of 4.4 °C and 1-butene which has a boiling point of -6.3 °C.

The invention in one aspect, is particularly suited to cause such separation. Other important diene\mono-olefin separations include separation of hexadiene from hexene and separation of octadiene from octene. In the process of the invention, the diene is separated from a mixture comprising the diene by contacting the mixture with an adsorbent which preferentially adsorbs the diene. This produces a non-adsorbed component and a diene-rich adsorbed component.

In one aspect, the adsorbent comprises an ion-exchanged zeolite X, zeolite Y, and/or zeolite LSX. The selected zeolite has exchangeable cationic sites, with silver cation or copper cation present at some or all of the exchangeable cationic sites. Substantial cation exchange is preferred so that at least half of the cationic sites of the ion exchange zeolite contain a copper or

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silver cation. It is preferred that the ion exchange be . 2 1000 particles y substantially or essentially complete so that the silver or copper ion exchange level of the exchangeable ion content is substantial enough to change the characteristic. In the case of the silver ion-exchanged zeolite, desirably a silver ion exchange level of the which is at least 70%, more desirably at least 80%, most desirably at least 85%, preferably at least 90% and more preferably at least 95% Most preferably, 10 substantially all (i.e. 99%), of the exchangeable ion sites Alternatively, the Xzeolite, Y-zeolite or zeolite_LSX is a copper ion-exchanged and the ion exchange be as V : Lord bash complete as described immediately above with respect to the Description silver cation is That is a at least half of the cationic the copper ion exchanged zeolite are occupied by copper copper. In the case of copper ion exchanged zeolite, the same level of high exchange content applies, according to to a secretary progressive levels stated above for silver. www.20 preferred that essentially complete ion exchange occur at 10. 100 - whereby substantially all (i.e., 99%) of the exchangeable * in I consecutionic sites are occupied by copper cations.

The copper and silver ion exchanged zeolites approvide a junique advantage in that diene\mono-olefin 25 separation is facilitated by formation of π-complexation bonds. Therefore the silver ion exchanged zeolite, when complexation bonds for releasibly retaining the targeted unsaturated hydrocarbon desired to be selectively removed.

30 By formation of π-complexation bond, the silver or copper ion exchange zeolite is able to retain the targeted to pressure. Thereafter the silver or copper ion-exchanged pressure are changed to exchange the adsorbed targeted hydrocarbon when a si35-id-either or both of temperature and pressure are changed to see cause desorption (release).

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so specialisms of a targeted unsaturated hydrocarbon compound is achieved by contacting The the date mixture containing the targeted compound with an absorbent which comprises a type A zeolite. The type-A be zeolite is usable in its calcium form. The type A zeolite siz do may also be used for selective adsorption where metal dations seffected from the group of alkaline metal cation terms and alkaline earth metal cation are present. Therefore, which the Type A zeolite may be represented by the nominal 10 general formula $M^{41}_{x}Z^{42}_{y}A^{43}_{b}[(AlO_2)_{12}](S1O_2)_{12}]$ wherein M^{41} is an end of alkali cation, Z'asis an alkaline earth cation, and A' is be and we are a tri-valent cation, the value of x is 0 to 12, the value es of your of your of to 6, and the value of b is at minimum zero and at maximum less than the sum of a plus y, provided that: x ohalance 15 wid 4 2y 43b fs 12. For charge balance the maximum walue of of the is is is in it is preferred that bis less than 4. alkaline metal cation disted from lithium, sodium, of gradesons potassium, Frubidium and caesium and mixtures thereof and the alkaline earth metal cation is selected from the group consisting of beryllium, magnesium, calcium, strontium, Marium and mixtures thereof The trivalent cation is with the ferably a metal compound capable of a trivalent valence astilities for condition: Examples include aluminum and boron.

invention are used in a method for separating an unsaturated hydrocarbon from a mixture by accomplishing adsorption at a first selected pressure and temperature and then accomplishing release of desorption by changing at least one of the pressure and temperature. Preferential absorption is achieved at a pressure greater than the desorption (release) pressure. Preferential absorption pressure may be as high as about 35 atmospheres or more; and the desorption pressure of preferential adsorption is a thought atmosphere and the pressure of preferential adsorption is a thought atmosphere and the pressure of preferential adsorption is in a range of about 1 atmosphere to about 35 atmospheres; and most desirably about 1 to 2 atmospheres. Desirably, the

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pressure of release is in a range of about 0.1 atmospheres to about 5 atmospheres; and most desirably in a range of about 0.1 atmospheres to about 0.5 atmospheres. The temperature of preferential adsorption is desirably selected to be in the range of about 0°C to about 150°C; more desirably up to about 120°C and most desirably in a range of about 25°C to about 80°C. The temperature of release is desirably in a range of about 70°C to about 25°C, and most desirably about 100°C to about 120°C.

The invention provides substantial advantages over conventional methods for separating dienes from a mixture due to the effective and economical process and adsorbents provided by the invention.

objects, features and advantages of the invention include an improved method for separating diene from a mono-olefin in a mixture, and particularly for separating C4 to C8 diene from a mixture which includes corresponding C4 to C8 mono-olefin. Another objective is to provide new adsorbents used in such new separation method.

These and other objects, features, and advantages will become apparent from the following description of the preferred embodiment, claims, and accompanying drawings.

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BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows line representations structure: (a) Solidate cage; or truncated octahedron; (b) type A zeolite "unit cell" (c) "unit cell" of types X and 5 Y, or faujasite; (d); cation sites in type A (there are eight I, three IF, and twelve III sites per unit cell); (e) cation sites in types X and Y_S (16 I, 32 I', 32 II, 32 II', 48 III, and 32 TII's sites per unit cell)

Figure 2 shows the pure-component 10 isotherms of 1,3-CH6 mand slack, on NaY and NaLSX type zeolites at 70 %; section lanci som

Figure 3 shows uptake curves for 1,3-C4H6 and 1-C4H8 on

Nay-type zeolites. sor ye bedayon a someonent equilibrium isotherms for 1,3-CiH, and 1-CiH, Agy zeolite at 70°C and

25°C. 25°C. Figure 5 shows the equilibrium isotherms of C2H4 on NaY

and Agy type zeolites at 70°C. Figure 6 shows low pressure equilibrium isotherms for

20 1,3-C,H, and T-C,H, on 5A zeolite at 25°C.

20 1,3-C,H6 and 1-C,H8 on right of showshup take curves for 1,3-C,H6 and 1-C,H8 on Sr exchanged 5A and 5A zeolites measured at 70°C. Commission of Spring

Figure 8 shows desorption curve for temperature driven release of 1,3-C4H6 from 5A zeolite.

Figure 9 shows equilibrium adsorption isotherms for C_4H_6 on AgY and NaY at 120°C.

Figure 10 shows low pressure equilibrium isotherms for $1.3-C_4H_6$ and $1-C_4H_8$ on 5A at 70°C.

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DESCRIPTION OF THE PREFERRED EMBODIMENTS

The invention provides improved methods and adsorbents for separating a diene from a mixture which includes such diene. The invention is particularly useful for separating dienes having four to eight carbons from corresponding mono-olefins having four to eight carbons. Improved separation methods are needed due to the close boiling points of the "C4" toNoC8 dienes and corresponding C4 to C8 mono-olefins Selected examples are as follows with numerical values being the boiling points in degrees centigrade 1,22 and 1,3-butadiene respectively 10.8 and -4.4; 1-butene, 2-butene cis and trans, respectively -6.3, 3.7 and 0.9; 1,3-, 1,4-, 1,5- and 2,4hexadiene respectively 73, 65, 59,5, and 80; 1-hexene, 2hexene cis and transmand. 3-hexene cis respectively 63.3, 68.8, 68, 66.4 and 67.1; and 1,7- and ij Nidae.**15**a 2,6- octadiene at 113-8 and 118-20; and 1-, 2-, 3-, and 4octene in a range of 121.3-125:6; all according to the 62nd

20 To one embodiments there is provided a process for separating diene from a feed mixture comprising the diene and at least one other unsaturated hydrocarbon compound, where the process comprises contacting the mixture with a diene selective adsorbent which is an ion-Plant 25 exchanged zeolite. Desirably, the ion-exchanged zeolite is The lower limit a Y zeolite, X zeolite, and/or low silica X zeolite, (LSX). Most desirably, the exchangeable cationic sites of the zeolite are ion-exchanged with silver cation or copper cation. It is most preferred that the zeolite be a silver 30 zeolite (Ag-zeolite). The character of these zeolites will be described more particularly below. In the case of type LSX zeolite, it is preferred that it have a silicon to It is most 10 boversed as aluminum atomic ratio of sless than 1.2. dollar sations a preferred that the ratio of Si/Al be about 1.

It is desirable that more than half of the ion

the case of Ag-zeolite. It is preferred that in the case

exchange sites of the zeolites contain the silver cation in

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of Ag zeolite substantially all of the cation sites are occupied by silver in a +1 oxidation state (+1 valence state) . In the case of Cu-zeolite, it is also desirable that more than half of the ion exchange sites contain copper ions. It is also preferred that substantially all of the sites are ion exchanged with copper in the case of copper exchanged zeolites where the copper is in the +1

valence or oxidation state. o same invention provides a process for causing the separation of diene from one or more other unsaturated hydrocarbons, particularly monoolefin as described above, using a type A zeolite. In this process the diene is separated from a feed mixture utilizing the type A zeolite having an alkali-metal cation or an alkalines earth metal cation at exchangeable cationic sites to cause the

adsorption of the diene.

Desirably: commercially available 5A zeolite is The 5A zeolite contains calcium (Ca) as the major used. Bascory a feet. cation. This means that for all the available cation sites of A-zeolites Ca is found at over half such sites. minor Cation diss sodium. Therefore, the 5A zeolite has substantially and essentially all of its cationic sites occupied by Ca and Na, but primarily Ca. This 5A zeolite is also referred to herein as CaA zeolite.

In one embodiment, the type A zeolite optionally contains a mixture of cations besides the alkali metal and alkaline earth metal. Therefore, at some of the cation exchange sites of the zeolite, cations other than +1 and +2 will be present. The nominal formula of this zeolite is M⁺¹_xZ⁺²yA⁻³_b[(AlO₂)₁₂ (SiO₂)₁₂] wherein the value of x is 0 to 12 and the value of y, is 0 to 6, and the value of b is at minimum zero and at maximum less than the sum of x plus y, provided that: x, tr2y +3b is 12. This is believed to provide a mixture of cations in this type A zeolite which is balanced. It is preferred that when the A zeolite contains tri-valent (+3) cations, the atomic amount of such

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tri-valent is less than the combined amount of the alkali and alkaline metal cations. It is most preferred that in the aforesaid nominal general formula, the alkaline earth metal is primarily Ca, providing Ca-A (5A) zeolite.

The method and adsorbents (sorbents) of invention are particularly suited for temperature swing adsorption (TSA) and pressure swing adsorption (PSA). process is effective to separate diene from a mixture containing one or more other unsaturated hydrocarbons and particularly emono-olefin compounds. Before describing the invention and the use of zeolites of the invention Sin TSA and PSA processes, more particular description of the physical characteristics of the zeolites of the invention is provided along with preferred ion exchange method. . apsc. dess siblique

adsorbents due their selectivity. Zeolites selectively adsorb molecules on the basis of the size and the shape of the adsorbate molecule and are therefore called molecular sieves. Zeolites have been known for use in selective hydrocarbons. adsorption of carbon monoxide and Crystalline zeolite Yww zeolite A and zeolite X described in USPN 3,130,007; 2,882,243; 2,882,244; eachsof which is incorporated by reference in its entirety. Type 5A zeolite, and type 13X zeolite are described for nitrogen adsorption in USPN 5,551,257. Types 4A (Na-A) and 5A (Ca-A) zeolites, are described in USPN 3,785,122: Low silica X zeolite (LSX) having Si/Al ratio less than or equal to 1.25 desirably less than or equal to 1.2, and preferably about 1 is described in USPN 5,268,023. Each of the aforementioned patents is incorporated herein by reference in its entirety. Consistent with the features described in these patents, zeclite characteristics are below excerpted from d'Gas Separation Processes by R.T. Yang (1987; Butterworth Publishers). 7.0

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Zeolites are crystalline aluminosilicates of alkali or alkali earth-elements such as sodium, potassium, and calcium, represented by the stoichiometry:

M_{x/n} (AlO₂) (SiO₂) | zH₂O

where x and y are integers with y/x equal to or greater than 1, n is the valence of cation M, and z is the number of water molecules in each unit cell. are shown in Figure 1(b) and (c). The cations are necessary to balance the electrical charge of the aluminum atoms, each having a net charge of -1. The water molecules can be removed with ease upon heat and evacuation, leaving an almost unaltered aluminosilicate skeleton with a void fraction between 0.2 and 0.5. The skeleton has a regular structure of cages, which are usually interconnected by six rate dropping sig windows in each cage. The cages can imbibe or occlude large amounts of guest molecules; in place of water. size of the window apertures, which can be controlled by fixing the type and number of cations, ranges from 3 Å to 10 A. The sorption may occur with great selectivity because of the size of the aperture (and to a lesser extent because of the surface property in the cages) - hence the name molecular sieve.

At least forty species of naturally occurring zeolites have been found The principal chabazite, (Ca, Na₂) Al₂Si₄O₁₂(6, H₂O); gmelinite; (Na₂, Ca) $Al_2Si_4O_{12}$ (6 $H_2O)$; mordenite; (Ca, K_2 , Na₂), $Al_2Si_{10}O_{24}$ (6.66 H_2O); levynite; $CaAl_2Si_3O_{10}$ (5 H_2O); and faujasite, (Na₂, Ca, Mg, K_2)OAl₂Si_{4.5}O₁₂ (7. H_2 O)... Mere than 150 types of zeolites have been synthesized; they are designated by a letter or group of letters - Type A, Type X, Type Y, Type ZSM, and so on. The commercial production of synthetic zeolites started with the successful development of low-temperature (25-100°C) synthesis methods using very reactive materials such as freshly coprecipitated gels or amorphous solids.

The primary structural units of zeolites are the tetrahedra of silicon and aluminum, SiO4 and AlO4. units are assembled into secondary polyhedral building

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units such as coubes, hexagonal prisms, octahedra, truncated octahedrates The silicon and aluminum atoms, located atothe corners of the polyhedra, are joined by a shared oxygen . The final zeolite structure consists of assemblages of the secondary units in a regular threedimensional crystalline framework. The ratio Si/Al is commonly one to five The aluminum atom can be removed and replaced by silicon in some zeolites, thereby reducing the number of cations; and the cations can also be exchanged. 10 % The inner atoms in the windows are oxygen. The size of the windows depends, then, or the number of oxygen atoms in the . St. L. Trade Frings - S. four, Flive, Tsix, Teight, Tten, por twelve. aperture size, as well as the absorptive properties, can be same of suffurther modified by the number and type of exchanged eations A description of the structures will be given only for the zeolites important in gas separation, Type A where the and Type X sand Yt. (See Table, The trop to a wear and

Type A. 2 Type A. 2 The structural unit in Type A. zeolite, as well as in Types X mandally is is the truncated octahedron, 20 shown in Figure: 1 (a): This unit is also called sodalite cage, as sodalite is formed by directly fusing the fourbuy 300 member rings of the units. Two The four-member rings of the socalite units cantalso be linked through four-member prisms, as shown in Figure 1(b), which is type A zeolite. 25 The unit cell of Type A zeolite, as shown in this figure, contains 24 tecrahydra, 12 AlO, and 12 SiO, When fully water molecules are contained in the central cage or cavity of the unit cell, and in the eight smaller sodalite cages. The free diameter in the central cavity is 30 ... 11:4 A, which is entered through six eight-member oxygenring apertures with a minimum diameter of 4.4 Å. There are twelve negative charges to be balanced by cations in each unit cell. The most probable locations for the cations are indicated in Figure 1 (d) TType Inds at the center of the The six member ring, thus at one of the eight corners of the cavity. Type II is at the eight-member aperture, directly obstructing the entrance. Type III is near the four-member -16" - 25 **15**"

ring inside the cavity. Type: A zeolites are synthesized in the sodium form, with 12 sodium cations occupying all eight .. sites in Francethree sites sincliff, plus none site in III. This is the commercial Type AA zeolite, with an effective aperture size of 3.8 A. The sodium form can be replaced by various other cations or by ashydrogen ion. The commercial Type 3A zeolite wis formed by exchanging Na with K', resulting in a smaller effective aperture size due to the larger K. The aperture size of the sodium form can also 10 be increased by exchanging Nat, with Cator Mgt2, since 2 Nat are replaced by one bivalent cation. The form of the exchanged Ca⁺² or Mg⁺² is Type 5A with rather unobstructed and larger apertures; established larger apertures; established larger apertures.

Types X and M. The skeletal structure of Types x and Y zeolites are the same as that of the naturally occurring faujasite. The sodalite units are linked through six-member prisms as shown in the unit cell in Figure 1(c) SK-Each unit cell contains 1925(Si, Al)O4 tetrahedra. newhere of the aluminum lons per unit cell varies from 96 to 77 for Type X zeolite, and from 76 to 48 for Type Y Fzeolite Frimework has the largest central cavity volume of any known applite, amounting to about 50% void Secusion in the dehydrated form, the unit cell, when fully ** The third ated, Acontains approximately: 235 water molecules, 25 25 mostly in the center cavity. The aperture is formed by the ville is if twelve-member oxygen rings traith to require of approximately 744 A. Three major locations for the cations The locations are: center of The bix-member prism (I) and opposite to I in the sodalite cavity (IP and II'); and at the twelve-member aperture (III and III') ... The commercial 10X zeolite contains Ca+2 as the major cátion, and Natis the major cation for 13X zeolite. The distribution of Nat, $K^*_{\gamma\gamma\gamma}$ Cather cations, and H_2O in 35 $^{-1}$ X and Y zeolites of the BET surface area measured with N₂ for zeolites falls in the range between 500 and 800 m²/g.

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In one aspect, adsorbents of the invention, as described below, achieve selective adsorption by means of the \$\pi\$-complexation mechanism. Separation by \$\pi\$-complexation is a subgroup of chemical complexation where the mixture is contacted with a second phase, which contains a complexing agent. The advantage of chemical complexation is that the bonds formed are stronger than those by van der Waals forces alone, so it is possible to achieve high selectivity and high capacity for the component to be bound. At the same time, the bonds are still weak enough to be broken by using simple engineering operations such as raising the temperature or decreasing the pressure.

The m-complexation generally pertains to the main group (or d-block) transition metals, that is, from Sc to Local Cu, Y to Ag, and La to Au in the periodic table. These metals or their ions can form the normal so bond to carbon and, in addition, the unique characteristics of the dorbitals in these metals or ions can form bonds with the unsaturated hydrocarbons (olefins) in a monclassic manner.

This type of bonding is broadly referred to as m-complexation, and has been considered for gaseous hydrocarbon separation and purification using cumbersome liquid solutions.

2500 conventional π -complexation sorbents did not provide a large working capacity for the target olefin. The examples below show that the sorbents of the invention have superior selectivity for 1,3-butadiene adscription. The examples show the new adsorbents (sorbents) usable with preferred PSA and TSA processes for very effective diene separation. The PSA process is effectively usable with the new sorbents of the invention. Here, multiplicity of

periodic steady states is, an important aspect of cyclic adsorption process. For pressure swing adsorption (PSA), multiple steady states exist for a fixed set of operating conditions, over a particular range of one or more of these operating variables (i.e., bifurcation variables). The

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which component separation is conducted by pressure swing adsorption (TSA) and temperature swing adsorption (TSA).

Other less commonly used processes are volume swing adsorption and concentration swing adsorption. The most commonly described are PSA and TSA systems.

more readily adsorbable component and a less readily adsorbable component and a less readily adsorbable component is passed through an adsorbent bed capable of selectively adsorbing the more readily adsorbed component at an upper adsorption pressure. The eless readily adsorbable component passes through the bed and is readily adsorbable component passes through the bed and is depressurized to a lower desorption pressure for desorption of the more readily adsorbable component, and an account to the readily adsorbable component, and an account to the readily adsorbable component, and an account to the readily adsorbable component, and account to the readily adsorbable component.

*** 20 * best In temperature swing adsorption processing the European Pladsorbent is exposed to the feed mixture for a period of sweare life time during which the more readily adsorbed component is Thereafter the flow of the feed is shut off from adsorbed. and the adsorbent bed and the adsorbent is exposed to a purge 50:25 Fluid, typically a gas, which strips the adsorbed component configure of from the bedrand regenerates the bed for further use. TOWN STRANGER adsorbed component is driven off from the bed by as lightles wheating withe adsorbent in the Wregeneration state. Therefore, the temperature of desorption is higher than the temperature of the adsorption portion of the cycle. 6 3 00 00 Details of PSA and TSA adsorption will not be repeated The states where, as they may be found in the following United States price in Patents, each of which is incorporated by reference herein, ; 7 835; 7 75,672,196; 75,672,196; 800708 ybreca signiinm

Ion exchange of zeolite is easily accomplished by mixing the zeolite in an aqueous solution of the metal

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salt. The metablof the salt is the metal to be exchanged into the cationic site. The concentration of the solution is varied according to the desired level of ion exchange. Fig. 1. The ion exchanged recliter is other removed by filtration from the aqueous solution and washed free of the soluble salts This batch ion exchange is widely used due to its simplicity: Essentially complete ion exchange can be achieved by repeating the same procedure several times. By such repeated treatments over 90% of the exchangeable 10 cationic sites are consexchanged with Ag. Preferably, Sover 95% of such sitescare ion exchanged. The same high TO CONTROL OF Exchange his tobtainable with the copper ion at The Agreeolites of the invention were prepared by ion exchanging with assolution of AgNO, containing five 15 times the cationic exchange capacity of the zeolites. was done to assure complete ton, exchange. The Cu-zeolites bild with own of the finvention were prepared by ion exchanging with a solution of CuCl2 or Cu(NO3)2, followed by reduction of Cu+2 to algeria white currence was false of the early standards

20 20 The The fellowing examples show new sorbents for the challenging separation of removing trace amounts of dienes (50 PPM) from a normal alphasolefin (NAO) stream. sorbents of the wexamples below demonstrate operability for a pressure swing adsorption (PSA) or temperature swing m % -25 color adsorption (TSA) model. The ferre has surfaced

garage were pre-selected and weak chemical complexation. The first type of interaction derives from the molecular sieving effects of certain substrates such as zeolites or carbon molecular sieves (CMS): However, zeolites were mainly considered for this application due to atheir high Henry(s adsorption. For this approach; the small differences in TO THE Rinetic diameters of mono-olefin are exploited. saccomplished by exchanging cations of various sizes into To noddstroomthe pore-aperture of type A zeolites.

ក្នុងស្នើឡាង ខេត្ត ព្រះជាងការស្រាស់ ស្រាស់ សម្រ

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A A ISA STORE OF A POST Due to the obefinidenature of the components Tylic: Alinvolved in the examples, weak chemical and complexationbased sorbents that have demonstrated the capabilities of 178257.17 adsorbing olefin over paraffins are not necessarily suited * the 5 % for diene separation from Imono to lefting In the separation of diene from mono-olefin, both adsorbates are olefinic in The state of the s the double bonds am Double bonds that alternate with single widesproduce bonds are said to beaconjugated, double bonds that are State 10 and separated by more than one single bond are said to be Fisolated. A third, eless important class of dienes contain cumulated double bonds, that is, double bonds adjacent one were francther and sknown as altenes, of One of the most common dienes is 1,3-butadiene ... Its boiling point is -4.4%C and This 15 dery close to 1 but energy 6 lose to 1 but energy 6 3 Characteristics of these two Parallica Compounds is very difficultadue to their close boiling a major difference between the two is the This is a conjugate wdiene , natures of 1,3-butadiene. Since 1,3 Date so butadiene is present in such low concentrations, the bond 20 between the sorbate and the adportent must be very strong sensible to adsorbesignificant amounts of butadiene at such - That islow partial pressures lame on a monde extra og ... To will have the stant In the examples witowas shown that the properties

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cations and substrates. When dealing with bulk separations, high amounts adsorbed at dow pressures are usually not desired, and are usually avoided because they limit the working dapacity of the adsorbent. However, for this particular application, a high Henry's law constant is required. Therefore, zeolite-based sorbents are a good candidate for substrates. It is shown that Ag' exchange Y zeolite has high affinity for olefins at very low pressures. Therefore, the examples focus on using zeolitic materials such as Type A, X, or Y, ion exchange with Cu' or Ag' cations to carry out the separation of 1, 3-butadiene from 1-butene. It should be noted that the separation of the conjugated butadeine from butene is merely exemplary.

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The processes described below are also applicable to separate other dienes such as hexadiene and octadiene from mixtures containing hexene and octene. The temperatures and pressure given below are also exemplary.

Depending on the chosen conditions, the separation is accomplished in the gas phase, the liquid phase or some combination thereof, including for example, saturated gas. It should be noted that the butadiene and butene of the examples share common chemical characteristics with other diene/mono-olefin combinations described earlier. Therefore, the effectiveness of the invention in separating all such stated combinations is apparent.

The sorbents described in the examples below 15 contained various cations included in high surface area substrates. The dispersion of cations was accomplished using ion exchange. The chemistry of ion exchange in zeolites is well documented. See USPN 2,882,243, 2,882,244 and 5,268,023, each of which is incorporated 20 herein in its entirety. All exchanges were performed similarly. They involved vacuum filtering and washing of the zeolite with deionized water. Compared to the original cation exchange capacity (CEC), each solution contained 10fold cation equivalents. This procedure ensured 100% exchange. For A (Linde), LSX (low silica X, UOP), and Y (Strem Chemicals) zeolites, the starting forms contain Na*. The zeolites used were powder form (binderless). Prior to use the samples were calcined in vacuo at 350°C.

In the examples below, the hydrocarbons used as the adsorbates were 1,3 butadiene (CP grade, Matheson), 1butene (CP grade) and helium (pre-purified grade, Metro The gasses were used without further purification. Isotherms and uptake rates were measured 35 utilizing both a Shimadzu TGA-50 microbalance system following well known procedures. For low pressure data (<0.05 atm), a Micrometrics ASAP 2010 pore size

distribution analyzer was utilized. This system is capable of accurately measuring pressures in a range between 1 x 10⁻⁷ - 1.25 atm. While one can obtain data at very low pressures with the Micromeritics ASAP 2010, this is very time consuming. The Shimadzu TGA-50 thermogravimetric analyzer is used to screen potential sorbents. Also, measurements were made at two temperatures (25°C, 70°C) in order to obtain isosteric heats of adsorption. The overall diffusion time constants, D/R, were calculated from the uptake curves measured from a stepped pressure increment from 0. to 0.6 atm by well known methods and assumptions.

Example 1

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Pre-screening of Y-type Zeolites
for 1,3-Butadiene Selectivity

The framework structure of LSX and Y-type zeolites resembled that of the naturally occurring faujasite (see Figure 1). The pores of these zeolites are made of 12-member oxygen rings. They have an aperture size of about 8.1 Å. They only differ in the ratios of Si/Al.

20 This ratio determines the number of Cations per unit cell and therefore has a significant effect on the adsorption properties. Y-type zeolites contain between 56 and 76 cation sites, respectively. It is because of the properties mentioned above that these zeolites were selected as substrates. The large size aperture facilitates the diffusion of large molecules such as 1,3-butadiene and 1-butene. Also, the large number of cation sites available for exchange with Cu1+ or Ag1+ helps increase the adsorption capacity.

The pure-component equilibrium isotherms of 1,3-C4H6 and 1-C4H8 on NaY and NaLSX type zeolites at 70°C are shown in Figure 2. The partial pressures ranged from .06 to 1 atm. While these pressures are outside the range of interest for 1,3-C4H6, they are useful for screening potential substrates and for determining capacities for 1-

C4H3. Themequilibrium data was fitted with the Langmuir isotherm model: Thesequilibrium amounts of 1:3-C.H. and 1to the second of CaHa adsorbed at \$70° Chatqleatm on NaY zeolite were 2.80 and . D 2.69 mmol/g respectively. This equals about 36 molecules 5: 27 5 do of 1,3-C4H6 and 34, molecules of 1-C4H8 per unit cell of NaYmake curves for 45, 3-C4H, and 1-C4H, on Naytype zeolites are shown in Figure 3. They were obtained by change in pressure from 0-0.06 atm. Both components diffused very fast Complete uptake was 10 sin achieved within 50 seconds 5 This was due to the very large ": pore aperture usize hof the NaY zeolite, about 7.4 A. Diffusion time constants, D/R2, were calculated by fitting coless and experimental adata swith with solution of the diffusion as a susaid , equation for spherical particles as described by Karger and Ruthwen in 1992: The values of D/R2 obtained for 1,3-C4H6 ennagency wo and 1 ac. Hecat 270°C . Were 7085 % 403 and 5.76 x 103 1/s, had discuss respectively sea The ratios of ather diffusivities is rather Told Tuesco small: (#31.3) for kinetic separation application. However, . We incomed favorable scharacteristic sof W-type Zeolite is its 20 20 srelatively high Henry's Law constant Just his indicates that the Yetype seolites have good affinity for C4's and are The continue also good candidates to constand Caustillings ាស់ ខុននេះ សមាជាមាន គេសេចដែលថ្ងៃ សេចនេះសមា ថា បុខាធារថា ១១ ១១៤ ខេត្ត ១០ ១៩៣១ដែល១០១

Example 2

As per Example 1, Y-type zeolites have a very provided which affinity for C4's at low pressures. Therefore, this material is a good substrate for T-buttene purification, and also for shexene and octene purification. In order to increase the affinity of the Nay zeolite for 1,3 butadiene, the Na's cation was fully exchanged by Ag's which is capable compounds. The pure component equilibrium isotherms for 1,3-C4H6 and 1-C4H6 Agy to she with a state of the state corresponds to a concentration equal to 10 PPM. The equilibrium amounts of

mirron and 1,3-C4H2 and 1-C4H, at:300C and impatms were measured at 2.8 and but we and 2.3 mmol/g wu These results are very interesting because Fig. 7. 7 & satchighthoadings it sappears that sexchanging, Na with Ag had takers a polesser effect on the amounts of it, 3-C. Haradsorbed.

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LYBY 1/5 1/40 50m aso Low-pressure 19.8-C4H6 and 1-C4H6 adsorption data: 1977 10 14,0 on AgY type zeolite at::70°C is also shown in Figure 4. ve in this Figure, ite cam be observed that at 70°C the amount of neter thought 1,3-C. Haradsorbed matris On PPM was eabout 100.5 mmol/g. This abic adamentamount mis somewhat asmall sauther amounts of 1,3-C,H, egyn : 10 everimproved by decreasing on the dadsorption temperature Jest Section isotherms for Dania To Action 3 C.H. on Agy type zeolite are shown in Figure 4 also. magash 2000 Although 1,3-C4H, adsorption did not improve in the region Mashardayof importance, alix 110% tous x: 10% (10:50:PPM), there was 15 gran increase in adsorption at higher loadings. . BASW BASK 15 1 15 1 15 The lacks of 153. C4H6 adsorbed in the slow pressure gedies as eregime with the decrease in temperature could be attributed Tay and the suito equipment error as It is possible for the Micormerities 表表的 21 图象 ASAP 2010 to cut off adsorption before uptake completion Fight .20 to enter particular opressure pointhif the system is toos slow

was building diffusing This possible error was corrected and a new E. F. D. E. E. Sequilibrium: Asotherm afor astra, C. H. Onc. AgYabzeolite test greated included as per an example which follows below. - Or his of the Adressmen THE REPORT OF THE PROPERTY OF THE PARTY OF T

enelje gri- **Example 3**-lime og desponintiskalitik sylvik i skill

Confirmation of Selectivity: Tag the

The resident to confirm they make ration activity The the sorbent, bit was tested with C2H4x2ats 70°C. or mylen equilibrium isotherms of C2H4 on NaY and AgYatype zeolites species of at 70%C are shown in Figure 5. In this figure, the effect aid, 30 of m-complexation can be clearly observed at low pressures. * However, at higher pressures, this effect is somewhat This phenomenon could be attributed to a . The stilling of the pore cavity of Y-type zeolite. SHowever, for this particular application, the behavior of the sorbent at A pur 35 monthigh loadings is not important air It is the low pressure to an owner, helifupa with a time or large retribution on

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behavior of the sorbent which is critical for this particular purification-type application.

Example 4

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A-Type Zeolite Selectivity for 1,3-Butadiene
The structural unit of Type A zeolite is the sodalite cage. The unit cell of Type A zeolite contains 12 AlO₄ and 12 SiO₄ (see Figure 1). There are twelve negative charges to be balance by cations in each cell unit. The free diameter in the central cavity is 11.4 Å (Yang, 1987). Access to the pores is restricted by 8-membered oxygen rings with a free aperture of 4.3 Å in the unobstructed Ca²⁺ (5A) form. This can be reduced to 3.8 A by exchanging with National to 3.0 A by exchanging with Kt. It, is this wide variation of pore sizes and smaller cavity size that makes

type A zeolites desirable for butadiene separation.

Commercially available (5A) Zeolite from Linde

Commercially available (5A) Zeolite from Linde

Was tested. Low pressure equilibrium isotherms for 1,3-C4H6

and 1-C4H8 on 5A at 25°C are shown in Figure 6. Equilibrium and 1-C₄H₈ on 5n at 20 m notified at 1.8 amounts of 1,3-C₄H₆ and 1-C₄H₈ at 1 atm were measured at 3.8 and 3:3 mmol/g, respectively. The low pressure adsorption of this material was excellent. At a concentration of 50 PPM, this material adsorbed 0.8 mmol/g of 1.3 C₄H₆. The working capacity of this sorbent between 50 and 10 PPM is also excellent. This was measured at approximately 0.7 25 mmol/g.

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Example 5
5A Zeolite and 5A Ion-Exchanged Zeolite Selectivity

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erit in article galeri This example builds on the success of 5A type zeolite in adsorbing 1,3-C4H6 at very low loadings. Here, the focus was to reduce 1-C,H₀ adsorption. As mentioned Restricted matricial replications and additional expension with the strategies to synthesize a sorbent for the strategies to synthesize a sorbent for this application was to use kinetic or steric effects to separate 1,3-C4H6 (butadiene). from 1-C4H6 (butene).

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ំអ្នកស្រាវជាង (១) នាំស្រាវិទ្ធា និយមម៉ាក្រា ក្នុងជា និង (១០) ប

Therefore, it is possible to limit 1-C4H8 adsorption by hindering its uptake or completely excluding it from the pore structure. This was accomplished by exchanging Ca+ cations in the pores of Type A zeolite with several cations of various sizes. The pure component equilibrium isotherm for 1,3-C4H6 and 1-C4H8 on Sr exchanged 5A at 25°C are shown in Figure 7. The pressure in this isotherm ranged from 1 x 10-5 to 1 atm. Equilibrium adsorption amount for 1,3-C4H6 on Sr exchanged 5A at 25°C and 1 atm was measured at 3.1 mmol/g. Although this sorbent showed excellent capacity at n in a pi you'ver isranes end of tere single dapate, do high loadings (≈ 1 atm), it did not adsorb significant from 8 you'verseas at a 100 sector of 100 se amounts of 1,3-C,H₆ in the 10-50 PPM regime. Uptake curves for 1,3-C4H6 and 1-C4H8 on Sr exchanged 5A and 5A were measured at 70°C and are shown in Figure 7. The values of D/R² for 1,3-C,H₆ and 1-C,H₈ on CaA were calculated at 1.07 x 10² and 7.30 x 10⁻³ 1/s, respectively. Diffusion time constants were also measured on Sr exchanged 5A and were calculated at 8.55 \times 10⁻³ and 4.06 \times 10⁻³ 1/s, respectively. Due to the larger radius of Sr²⁺ over Ca²⁺ (1.12 vs. 0.99 Å), a small reduction in 1-C₄H₈ uptake rates is observed. However, the reduction in 1-C,H, uptake is not significant enough for a kinetic separation scheme. If the ion exchange is performed with the next larger cation, Ba2+, with a radius of 1.34 A, the uptakes of both adsorbents are severely hindered. Therefore, it is questionable whether hindrance of 1-C4H₈ access to the pore structure of A type zeolites using simple ion exchange techniques is possible without also blocking 1,3-C4H6. The small difference in kinetic diameter between the two molecules is problematic. 30 Desorption experiments were carried out on 1,3- C_4H_6 on 5A zeolite at 70° C. However, these experiments were performed in the Shimadzu TG-50 TGA. Therefore, they do not include data below 0.06 atm. Equilibrium amounts of 1,3-C4H6 on 5A Zeolite at 70°C and 1 atm were measured at 2.81 mmol/g. After desorption, at 1 atm, the sample was exposed to a helium stream at 70°C to regenerate it. However, this procedure only removed 1.23 mmol/g which left

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1.58 mmol/g of $1,3-C_4H_6$. This final amount was removed by heating the sample to 180°C in the presence of helium. desorption curve is shown in Figure 8. As per the above examples, success has been achieved with 5A zeolite for 1,3-butadiene separation. It is not clear yet the reason for the success of 5A and the lesser performance of Sr exchanged 5A which is very similar structurally. The pore size of this zeolite determines dits effectiveness for C6 Lift. Longand C8 separation surgence arew and reduced the

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1,3 Butadiene/1-Butene Separation: π-Complexation Effects 74. 清楚 1951年 83 980 12 Insprevious examples there is shown 1,3-butadiene (C.H.) adsorption on AgY-zeolite at various temperatures. These examples did not include data to directly compare the 15_{\odot} effects of π -complexation on C_4H_6 adsorption. This example sw. some includes andirect comparisonaby measuring C.H. adsorption on the sodium-exchanged type Y zeolite (NaY) of It is known that the sodium cation is mot capable of π=complexating with olefins. A comparison involving AgA and CaA (5A) was not used because of the dominance of kinetic effects in the AgA system. The pore size of AgA lies in the range between 3A and 4A type zeolites.

> Equilibrium adsorption isotherms for C_4H_6 on AgY and NaY at 120°C are shown in Figure 9. The effect on π complexation is observed in the equilibrium amounts of C_4H_6 adsorbed on AgY and NaY at 1 atm which were measured at 3.3 and 2.6 mmol/g, respectively. However, the adsorption of C_4H_6 at 50 PPM of saturation pressure of 1-Butene (C_4H_8) at $120\,^{\circ}\text{C}$ (1.1 x 101^{-3} atm) is a more significant parameter. Using this parameter, the effects of π -complexation are The adsorption amounts of C_4H_6 at 50 PPM more significant. on AgY and NaY were measured at 2.7 and 0.3 mmol/g, respectively. The working capacity of the sorbents in the range of 50 to 10 PPM (1.1 x 10^{-3} - 2.2 x 10^{-4} atm) was calculated at 2.35 and 0.2 mmol/g, respectively. When the working capacities of the sorbents are calculated,

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superior performance of π -complexation sorbents becomes

Added isotherms were measured at 270 c. The isotherms are

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shown in Figure 10. The amounts adsorbed are lower at 70°C. More significantly, the heel of the isotherm for butadienes is shifted toward a higher partial pressure. Fortunately, however, the amount adsorbed is quite high at seques butadiene partial pressure of 50°ppm of 10°atm (i.e., the odd lad od saturation pressure of butene at 70°C. The amount is signed as a major mately 1 mmol/go The amount adsorbed at 10 ppm of 10 moint 15% atm sis mearly/zerosis Hence 5A zeolite is an attractive monal that sorbent for this selective removal of diene at 70°C (at a gradual pressure of 10°atm) atm pressure of 10°atm) atmosphere of the surface saw (AC) ascoluther zeolite is though to contribute to the separation.

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Table I. LSX, Y and A zeolite nominal chemical formulas more rife to concus praylland to the AgLSX AgLSX Age [(AlO2) ag (SiO2) ag] and the arm are are also as a feet along the arms. 100 មក្សាស្ត្រ ស ខេក្ស consit and nedsie viltug of beey belin Agy (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) 138 (\$102) ាន ខេត្តប្រំ យោម។ ក្រើ AULEIC domonacua cerriporti au an cefinaratira va co 5 CaA Ca₆[(AlO2)₁₂(SiO2)₁₂] odeli o w da delamento allo caralelo-pode escipto de esc Culsx Cu_s [(AlO2)₉₆ (SiO2)₉₆ eurratión be a i Naieliein Marata securarecamos mas Cu₅₄ [(AlO2)₅₄ (SiO2)₁₃₈] and ture to be concentrated to the contract of Mixed Metal A M*1 Z*2 A*3 [(AlO2)12 (SiO2)12] $\frac{1}{2} \left(\frac{1}{2} + \frac{2y}{4} \right) + 3b = 12$ To entrolation route ent of our controls aviangle listing 10 Note: In X-type zeolites, the AlO₂/SiO₂ ratio is greater than 54/138; and the total valence of the cations is equal to the number of Alo, units. si moni ensib sangireblob as denometratel hy vice emangle. Degend' g en the object andiations, the separation is accombined to the are search filteric with the end of the with the decidence is a common of the decidence of the contraction of ÷ 7, podestra lestrolded au responsariaded an en en el control de contr we are that the server is not been the real factor and the contract of Cti witnes fitti 64 to 1210 merè-piefika. Demont (121 bok Abortes as a contract of actions and actions of the contract o district a contract in apparation. Hereigh in the place is iden-ಳ"ದ ಇರಡಿ ಅರ್ಚಿತುಕ€ ದರ 1ಕರ್ತು - ಅಥವ ತನಸೆಗಡಳು ರುಗುಬರರು ದಗ್ಗ indian grade lugge sie odra frie brid respili quidemant of assuses for each ranging district from who is a companient programment of the companient of the companien spiralica ama santina en marcante de marcante de la comparció de la comparció

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The invention provides substantial over conventional methods for separating diene from a mixture. The adsorbents and methods of the invention are useful for purifying mono-olefin from a mixture which includes mono-olefin and diene. The adsorbents and methods can be used to purify either the dienesor to purify the mono-olefin. The adsorbents and methods as exemplified in the examples demonstrate particular effectiveness removing a diene from a mixture comprising the diene and one or more mono-olefins. The examples show effective separation results using gas-phase separation at the pressures and temperatures stated therein. The adsorbents and processes are demonstrated for a saturated 1-butene (olefin) stream, which is contaminated with 1,3-butadiene (diene), typically at one weight percent or less. separation in this case may include both gas and liquid phase selective adsorption due to the saturated nature of the 1-butene olefin stream. The processes described herein are described with reference to separation of C4 to C8 diene from a C4 to C8 mono-olefin. The physical characteristics of the adsorbents result in very effective separation as demonstrated by the examples. the chosen conditions, the separation is accomplished in the gas phase, the liquid phase or some combination thereof, including, for example, saturated gas. reasons described above, the adsorbents are also considered to be useful for separation of other dienes, that is C4 to C10 dienes from C4 to C10 mono-olefins. Beyond C10 the process is also thought to be applicable, for example, C12 diene/C12 mono-olefin separation. However, the selectivity and economic benefits are expected to decline for the higher hydrocarbon mono-olefin/diene separation.

> The invention provides good results at operating temperatures and pressures that are not extreme. results are achievable at pressures on the order of subatmospheric (i.e., 0.01 to 0.1 atm) to moderately high (i.e. 20 to 30 atm) and in a pressure swing adsorption

method. Good results are achievable at temperatures from ambient or a desired feed temperature (i.e. 0 to 25°C) and up to moderately high (i.e. 250°C), and in a temperature swing adsorption method. With the adsorbents of the invention, temperature swing or pressure swing adsorption processes are usable for effective separation between dienes and mono-olefins. This is demonstrated by the very effective purification of butenes, by removing 1,3-butadiene at concentrations above 20 ppm to final concentration below 10 ppm. Therefore, the invention provides a very attractive solution to the problem of selective adsorption of trace amounts of diene to separate diene from a mixture

of certain embodiments thereof, it is not intended that it be limited to the above description, but rather only to the extent set forth in the following claims.

The embodiments of the invention in which an exclusive property or privileged is claimed, are defined in the following claims.

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sicers for ere exiltees noon the aimed is: 1. A process for separating a diene from a mixture including said diene; said process comprising the ${
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m tr}_{i$ contacting salid mixture with an adsorbent which preferentially adsorbs said diene, thereby producing a nonadsorbed component and a diene-rich adsorbed component, wherein said adsorbent comprises at least one of (a) and 13(1) (b) tydiege, at congenimatique spove, 20noiseavel sale , each (a) an ion-exchanged zeolite selected from the ic melders end to deliberate group consisting of zeolite X, zeolite Y, odrigon or contibute admiras costa file LSX, said zeolite exchangeable cationic sites, and emmed willedimmed and maintage of said sites having JI LENG ANDRESS IN LOS EL CATION OF COPPER CATION PRESENT; ed a contract to (b) type A zeolite having exchangeable cationic sites, a plurality of said A zeolite sites us spiny of orlineval educating at an alkalite metal cation ni beniget aus .benistred alkatine earth metal cation present.

2. The process of claim 1 wherein said mixture comprises at least one mono-olefin having as many carbon atoms as said diene.

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- 3. The process of claim 2 wherein said diene is selected from the group consisting of butadiene, hexadiene, octadiene and mixtures thereof; and said mono-olefin is selected from the group consisting of butene, hexene, octene and mixtures thereof.
- 4. The process of claim 2 wherein said monoolefin is butene and said diene is butadiene.
- 5. The process of claim 2 wherein said monoolefin is hexene and said diene is hexadiene.

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- 6. The process of claim 2 wherein said monoolefin is octene and said diene is octadiene.
- 7. The process of claim 2 wherein said mixture comprises said mono-olefin in a gaseous state and saturated with said diene.
- 8. The process of claim 1 wherein said type LSX zeolite has a silicon to aluminum (Si/Al) atomic ratio of less than or equal to 1.2.
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 9. The process of claim 8 wherein said ratio is main led to infer non-redia main so
- 10. The process of claim 1 wherein said X and Y resident zeolites respectively have a silicon to aluminum ratio of 1:1 and 1000:1.
- 11. The process of claim 1 wherein at least half of the cationic sites of said ion-exchanged zeolite contain said silver cation.
- 12. The process of claim 1 wherein essentially all cationic sites of said ion-exchanged zeolite contain said silver cation.
- 13. The process of claim 1 wherein at least half of the cationic sites of said ion-exchanged zeolite contain said copper cation.
- 14. The process of claim 1 wherein essentially all cationic sites of said ion-exchanged zeolite contain said copper cation.
- bus entractive in An in end tash to entract the process of claim 1 wherein said type A treatours of the process of claim 1 wherein said type A zeolite has the nominal general formula M*1 xZ*2 A*3 [(AlO2)12 (SiO2)12] wherein M*1 is an alkali metal cation, Z*2 is an

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alkaline earth metal cation, and A^{+3} is a tri-valent cation, $0 \le x \le 12$, $0 \le y \le 6$, and $0 \le b < 4$ provided that: x + 2y + 3b is 12.

- 16. The process of claim 15 wherein said A⁺³ is a metal cation and said zeolite comprises said A⁺³ in an a said atomic amount less than the combined atomic amount of said alkali metal cation and said alkaline earth metal cation. To older alkali metal cation and said alkaline earth metal cation.
 - 17. The process of claim 15 wherein the alkaline earth metal cation is calcium (Ca) and at least half of the cationic sites contain calcium.
 - 18. A process of separating a diene selected from the group consisting of butadiene, hexadiene, octadiene and mixtures thereof from a mixture including said diene, said process comprising the steps of:

contacting said mixture with an adsorbent which preferentially adsorbs and releasably retains said diene at a selected temperature and pressure, thereby producing a non-adsorbed component and a diene-rich adsorbed component, wherein said adsorbent comprises at least one of (a) and (b),

- (a) an ion-exchanged zeolite selected from the group consisting of zeolite X, zeolite Y, and zeolite LSX, said zeolite having cation exchange sites, a plurality of said sites having silver cation or copper cation present;
- (b) type A zeolite having cation exchange sites, a plurality of said sites having an alkali metal cation or an alkaline earth metal cation present;

and then changing at least one of said pressure and temperature to thereby release said diene-rich component from said adsorbent.

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The process of claim 19 wherein said first the process of claim 19 wherein said first the content of pressure is in a range of about 1 atmosphere to about 35 masses of the content of the

The process of claim 19 wherein said first the process of about 1 satmosphere to about 2 atmospheres. nestron setts blue to light that

The process of claim 19 wherein said second process of about 0.01 atmosphere to about 5 atmospheres.

32. The process of class 27 where to a dissective

The process of claim 19 wherein said second pressure is in a range of about 0.1 atmosphere to about 0.5 atmospheres.

33. The process of claim of wherean samathelity

temperature of preferential adsorption is a first temperature, and the temperature of release is a second temperature greater than said first temperature.

ost recin this action resolving as a famograph decime has the process of claim 24 wherein said first and drucks a stemperature is in a range of about 0°C to about 150°C.

temperature is in-a-range-of about 25°Catorabout 80°C.

Landren with a trepological Theoprocess of colaims 24 wherein said second of ACLAD was temperature is in a range of about 70°C to about 250°C. The about 100°C to about 250°C.

moisso smells with 28. The process of claim 24 wherein said second of the process of about 100°C to about 120°C.

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A process for separating 1,3-butadiene from secure of comprising 1,3-butadiene and at least one other of contacting said mixture with an adsorbent which preferentially adsorbs said 1,3-butadiene, said adsorbent which comprising a silver of copper ion-exchanged zeolite is as a selected from the group consisting of Y zeolite, X zeolite, low silica X zeolite (LSX), and combinations thereof.

Latin line misserw % 30.5. The process of Claim 29 wherein said zeolite and at comprises a pluratity of Cation exchangeable sites and at least half of said sites contain silver cations.

Buch a pure manda %431 to The process of claim 30 wherein essentially a the draw and mall popusaid cation to sites contain silver cations.

32. The process of claim 29 wherein said zeolite broose bise comprises amplifiality of cation exchangeable sites and at 2.0 process pleast half of said sites contain copper cations.

33. The process of claim 32 wherein essentially bedusise establicofisaid cationics sites contain said copper cations.

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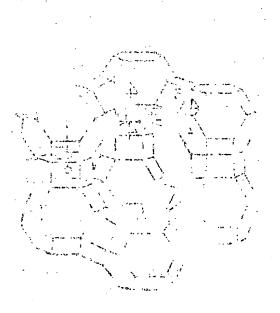
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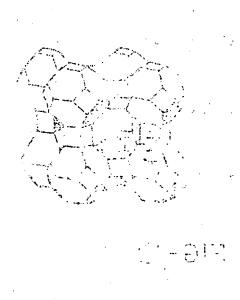
Entage and seasons 34. TA process for separating 1,3 butadiene from carmixture comprising 1,3 butadiene and at Teast one other C4 unsaturated compound, said process comprising the step of contacting said mixture with an adsorbent which preferentially adsorbe said 1,3 butadiene, said adsorbent comprising a type A zeolite having cation exchange sites, said is a appurality of said sites having an alkali metal cation or can an alkaline earth metal cation.

brokes of a largement of 35% a The process of claim 34 wherein the nominal contact argement formulas of said reolite list $-M^{+1}_{x}Z^{+2}_{y}A^{+3}_{b}[(AlO_{2})_{12}]$ (SiO₂)₁₂] wherein M⁺¹ is an alkali metal cation, Z⁺² is an the salkaline earth cation, and A⁺³ is a tri-valent cation, and S. Nowherein the value of x-is 00 to 12, the value of y is 0 to

6, and the value of b is at minimum zero and at maximum less than the sum of x plus y, provided that: x + 2y + 3b is 12.

36. The process of claim 34 wherein the alkaline earth cation is calcium (Ca) and more than half of the cation exchange sites contain calcium.





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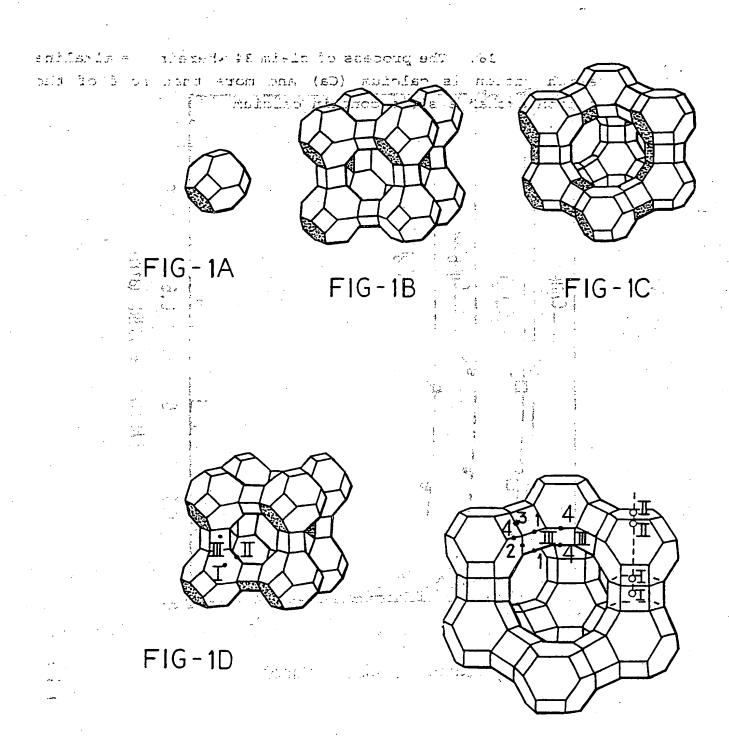
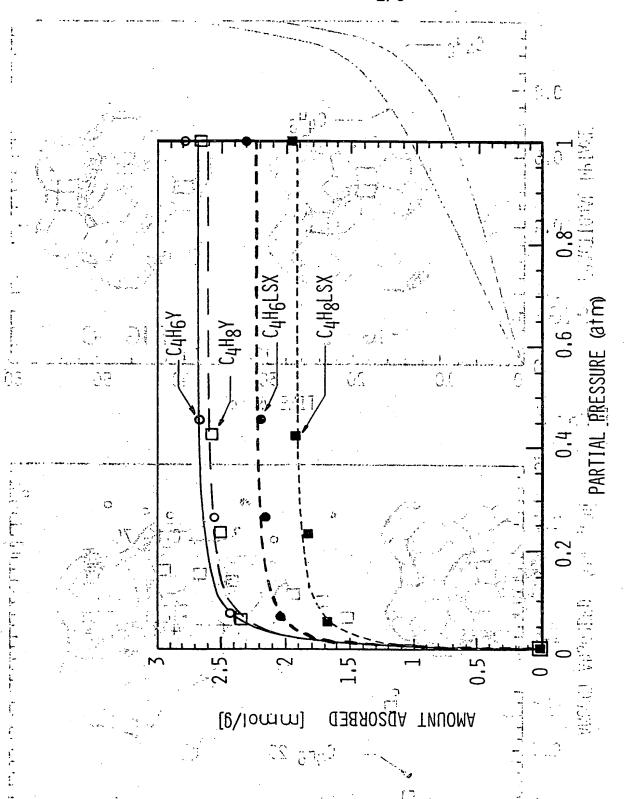


FIG-1E

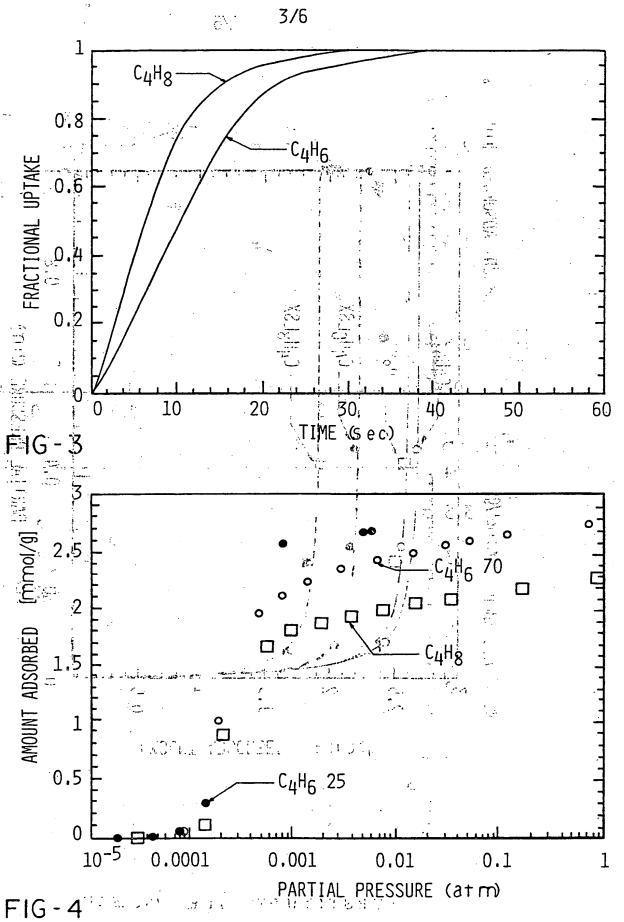
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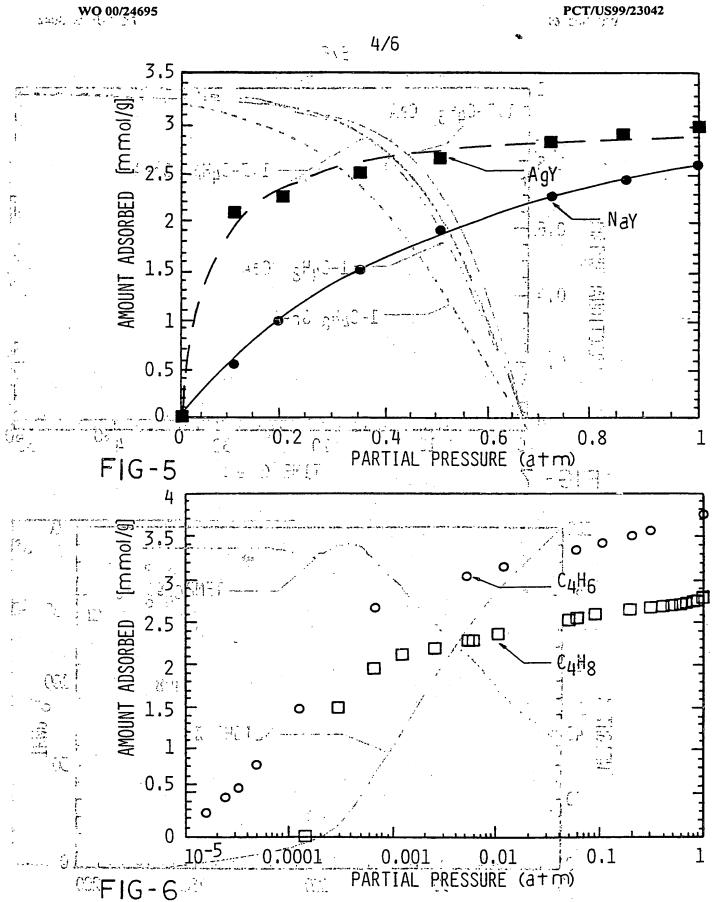
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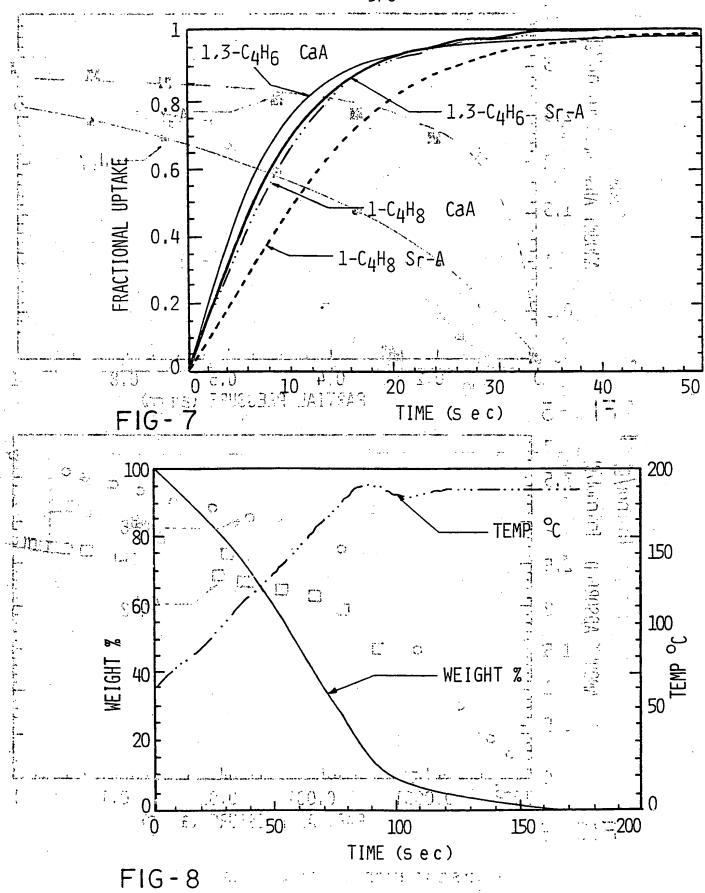
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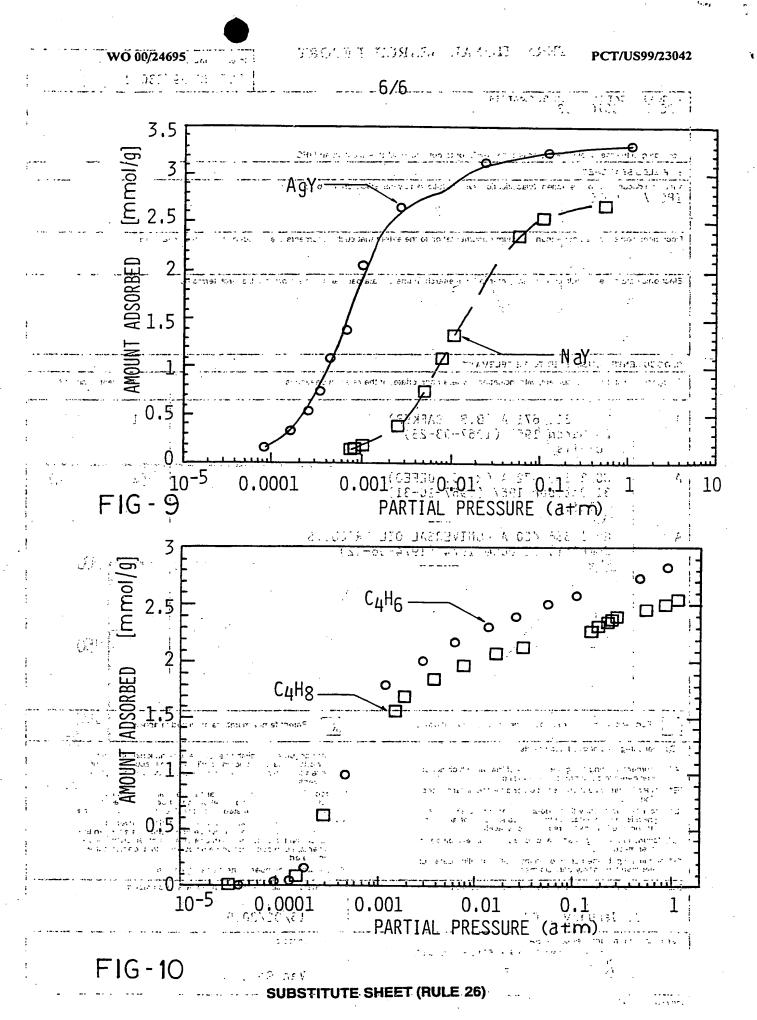




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Inter anal Application No

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A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C07C7/13	
According to International Patent Classification (IPC) or to both national classification	ation and IPC
B. FIELDS SEARCHED	
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C. DOCUMENTS CONSIDERED TO BE RELEVANT	
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Category Citation of document, with indication, where appropriate, of the rel	levant passages Helevant to daim No.
A US 3 311 671 A (B.B. BARKER) 28 March 1967 (1967-03-28) claims	
A US 3 350-472 A (R.J., DEFEO): (31 October 1967 (1967-10-31) chaims) 18923575 141774	$C = \frac{1}{1000 \cdot 100} \cdot \frac{1}{1000 \cdot 1000} \cdot \frac{1}{1000 \cdot 1000} \cdot \frac{1}{1000 \cdot 1000} \cdot \frac{1}{10000 \cdot 1000} \cdot \frac{1}{100000} \cdot \frac{1}{100000 \cdot 1000} \cdot \frac{1}{1000000} \cdot \frac{1}{1000000} \cdot \frac{1}{1000000} \cdot \frac{1}{1000000} \cdot \frac{1}{100000000} \cdot \frac{1}{100000000} \cdot \frac{1}{100000000} \cdot \frac{1}{10000000000} \cdot \frac{1}{10000000000000000} \cdot \frac{1}{10000000000000000000000000000000000$
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Further documents are listed in the continuation of box C.	X Patent family members are listed in annex
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Date of the actual completion of the international search 21 January 2000	Date of mailing of the International search report
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentiaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo ni, Fax: (+31-70) 340-3016	Authorized officer Van Geyt, J

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INTERNATIONAL SEARCH REPORT

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information on patent family members

Intern val Application No PCT/US 99/23042

Patent document cited in search report	Publi	cation	Patent famil	yl	Publication date	
US 3311671		3-1967	NONE	· · · · · · · · · · · · · · · · · · ·	1	
US 3350472	A - 31-10	 0−1967	NONE			
GB 1356420	A 1250	6-1974	NONE			
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